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PATENT

Docket No.: 97-2

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BY:

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Goldwasser et al.

Serial No.: 08/847,967

Filed: 4/22/1997

For: The Combinatorial Synthesis of Novel Materials

Group Art 1627

Unit:

Examiner: Baker,
M.

DECLARATION OF FRANCIS J. DI SALVO
UNDER 37 C.F.R. §1.132 IN SUPPORT OF
SUPPLEMENTAL RESPONSE H

I, Francis J. DiSalvo, hereby declare as follows:

1. I currently reside at 8 Sunny Knoll, Ithaca, NY 14850.
2. I am currently employed as the J. A. Newman Professor of Physical Sciences, Department of Chemistry and Chemical Biology, and as the Director, Cornell Center for Materials Research, at Cornell University in Ithaca, New York. My current responsibilities in these positions include research in the field of materials, including chemistry and solid-state chemistry, and teaching of several courses, including graduate level solid-state chemistry.

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I have been employed at Cornell University since 1986, and during this time have held various positions. My responsibilities during these positions included research in the field of materials, including chemistry and solid-state chemistry, and teaching of numerous courses, including chemistry and inorganic chemistry courses. Prior to joining Cornell University, I worked at Bell Laboratories for 15 years in various positions, including the head of the Solid State Chemistry Research Department, and the head of the Solid State Physics of Materials Research Department. I graduated from Massachusetts Institute of Technology (MIT) in 1966 with a bachelors degree (B.S.) in physics. I earned a doctoral degree (Ph.D.) from Stanford University in applied physics in 1971. Since obtaining my Ph.D., I have been continuously employed in the field of materials science research, and in particular, in the field of inorganic materials research. Further details of my academic training and work history are listed in my *Curriculum Vitae*, attached hereto as Exhibit A (Tab A).

During the period from about April, 1998 to present, I have served from time to time as a consultant and as a scientific advisor to Symyx Technologies, Inc. I do not currently own any stock options or hold any stock in Symyx Technologies, Inc. During this same period, I gained experience in the field of combinatorial materials science, including combinatorial (e.g., high-throughput) inorganic materials synthesis. This experience was derived in part through my consulting relationship with Symyx Technologies, Inc.

3. I am not an inventor of the subject matter claimed in the above-identified patent application.

4. In view of my training and experience, I am familiar with the level of skill in the art during the period of time that includes 1994, as well as the knowledge that would be attributed to what I understand to be a "person of ordinary skill in the art" at such time.

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5. I have studied the following materials in preparation for this Declaration: (1) the specification for the above-identified patent application, including the figures; (2) the currently pending claims, including independent claims 42, 68, 70, 72, 74, 84 and 88, as well as the claims depending therefrom; (3) the prosecution history to date; and (4) the references relied upon by the Examiner in the most recent Office action during prosecution of this application: U.S. Patent No. 5,356,756 to Cavicchi *et al.* and Fister *et al.*, Controlling Solid State Reactions Via Rational Design of Superlattice Reactants, pp. 155-234, Advances in the Synthesis and Reactivity of Solids, Volume 2, (JAI-Press, Inc. 1994).

6. It is my understanding that the inventions defined by claims 42, 68, 70, 72, 74, 84 and 88, together with claims depending therefrom are directed to methods for preparing arrays of diverse inorganic materials at discrete regions of a common substrate, and methods for using such arrays for identifying promising new materials. Each of the methods requires forming ten or more different materials at discrete regions of a substrate by a method that includes delivery of first and second components in successive layers within discrete regions of a substrate, while varying the composition, concentration, stoichiometry and/or thickness of the delivered components between respective regions. More specifically, each of the claims require (i) delivering a first component of the material to the substrate to form a first solid layer comprising the first component on the substrate, (ii) delivering a second component of the material to the substrate to form a second solid layer comprising the second component on the first layer, and (ii) varying the composition, concentration, stoichiometry or thickness of the delivered (first or second) component between respective regions. (See, for example, claim 68).

Additional features or steps are required in certain claims, including for example, forming an array of inorganic materials with delivery of five or more components for each of the ten or more materials (claim 70), forming one hundred or more inorganic materials on a substrate with a region density greater than 10 regions per cm^2 and allowing interaction of the delivered components, and then screening these inorganic materials for a property of interest and determining the relative performance thereof (claim 72), forming

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an array of composite materials, screening these composite materials for a property of interest and determining the relative performance thereof (claim 74), varying the composition, concentration, stoichiometry and/or thickness of the delivered components as a gradient between respective regions (claim 84), and forming a lattice or superlattice comprising the delivered components (claim 88).

7. My conclusion is that, based upon my review of the references listed under Tab B, and upon my understanding of the invention, in my opinion, at a time prior to October 18, 1994, a person of ordinary skill in the art of inorganic materials science would not have been led from these references to the invention set forth in claims 42, 68, 70, 72, 74, 84 and 88, and claims depending therefrom. That is, a person of ordinary skill that considered these references at such a time, alone or in combination, and in either case, together with the knowledge already possessed by such a person, would not have arrived at the invention defined by these claims. My analysis supporting this opinion is as follows.

8. The references relied upon in the most recent Office action are Fister *et al.* (1994) and U.S. Patent No. 5,365,756 to Cavicchi *et al.*

9. Neither the Fister *et al.* or Cavicchi *et al.* references disclose, teach or suggest at least one feature of the invention that I understand as being required by each of the claims - preparing arrays of diverse materials using a protocol that includes delivering components in successive layers within discrete regions while varying the composition, concentration, stoichiometry or thickness of a delivered component as compared between respective regions.

a. Fister *et al.* disclose a method for preparing a single material sample using a superlattice approach in which thin multilayer films are deposited uniformly on a single substrate. Subsequently, the film is processed at elevated temperatures to allow the interdiffusion and reaction of the species in each of the different layers. Fister *et al.*'s work appears to be aimed at separating diffusion and nucleation

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processes for research studies (*e.g.*, for examination of interfacial reactions on the atomic scale, nucleation of specific known phases, or formation of a metastable material). In this method, Fister *et al.* vary the delivered components sequentially in time, to form, prior to the subsequent processing, a lattice structure that is substantially the same across the entire sample substrate. There is no discussion of variations of delivered components across any layer of the film. Hence, the Fister *et al.* reference lacks any teaching relating to the preparation of arrays of diverse materials. In particular, Fister *et al.* does not disclose or suggest spatial variation of delivered components as compared between different discrete regions of a common substrate.

- b. Cavicchi *et al.* disclose fabrication of a plurality of micro-hotplates on a common substrate, each of which can be controlled independently from each other with respect to temperature and/or voltage bias. The reference discloses that the micro-hotplates can be used for process optimization by exploring the effects of locally-varying temperature and/or voltage conditions - particularly in connection with deposition studies and materials development (*e.g.*, film microstructure analysis, processing of high-temperature superconductors, thermal-fatigue testing, melt transition temperatures, gas-surface interaction studies, *etc.*). The reference also discloses end-use applications such as chemical sensors.
- c. Cavicchi *et al.* disclose, with reference to Figure 6, a sputtering process involving reactive RF sputtering in which a Sn target was sputtered in the presence of an oxygen and argon gas mixture. (See Col. 11, line 64 through Col. 12, line 3). Since this is a reactive sputtering process, a single component, the tin oxide reaction product, would have been deposited to the substrate to form a single film of tin oxide (*e.g.*, SnO_2). This process would not have taught or suggested any region-to-region variation in the composition, concentration, stoichiometry, or thickness of components as delivered to the substrate. Differences in the formed materials that would have resulted from the disclosed process, if any, would have been due to

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varying the temperature to which the delivered tin oxide films were exposed – not by varying the composition, concentration, stoichiometry or thickness of a delivered component between regions.

d. Cavicchi *et al.* disclose that after deposition of materials onto micro-hotplates at certain regions, the resulting materials can be subjected to various post-processing treatments that include the “subsequent deposition of additional materials”. (See Col. 10, lines 41-46). However, the Cavicchi *et al.* reference does not teach whether such additional materials are the same as or different from the earlier-deposited materials. In my opinion, a person of ordinary skill in the art would have understood this portion of the reference, when read in context, to teach deposition of additional materials for conventional purposes using traditional techniques (e.g., deposition of additional materials for device fabrication or to assist in bonding). Hence, this portion of the reference does not disclose or suggest controlling the relative composition, concentration, stoichiometry or thickness of the delivered components to vary between the ten or more respective regions.

e. Cavicchi *et al.* also disclose other conventional techniques for use in combination with their micro-hotplates. For example, Cavicchi *et al.* describe various photolithographic approaches to select certain micro-hotplates for deposition. (See Col. 10, lines 47-64 (conventional lithography), and Col. 10, line 65 through Col. 11, line 16 (maskless lithography)). However, Cavicchi *et al.* do not teach whether the materials deposited at the different regions are the same as or different from each other, and further, do not teach a deposition protocol that includes delivery of components in successive layers within discrete regions of a substrate, while varying the composition, concentration, stoichiometry and/or thickness of the delivered components between respective regions.

Additionally, a person of ordinary skill in the art would not have been motivated to apply the disclosed approach of Cavicchi *et al.* in a manner that would have led to

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the invention defined by the instant claims, since the selective lithographic approaches disclosed by Cavicchi *et al.* would have been understood to be a serial deposition processes that would have been less efficient and more complicated than just forming different materials on their own separate and distinct substrates. For example, forming an $n \times n$ array having n^2 materials according to the disclosed Cavicchi *et al.* approach would have been understood to require at least n^2 photoresist masking steps, at least n^2 material deposition steps, and at least n^2 photoresist removal steps (in total at least $3n^2$ steps) – which is even more complicated than the previous, traditional, individual n^2 material deposition steps on n^2 separate and individual substrates.

- f. Cavicchi *et al.* teach, *inter alia*, that multiple samples can be processed under a variety of temperatures and/or voltage bias conditions. This teaching, however, does not necessarily lead to the conclusion that multiple samples would be formed with varying compositions. Although it is possible that variation of process conditions could, in some instances, have some marginal affect on composition, such process variations could also have no affect on material composition, or may affect factors other than composition (e.g., morphology or grain size). In any case, such disclosure would not have taught or suggested to a person of ordinary skill in the art to vary the composition, concentration, stoichiometry, or thickness of the components being delivered to the substrate, as compared between regions.
- g. The Cavicchi *et al.* Abstract states that "(m)aterials are deposited onto pixels with individually controlled deposition conditions (pixel temperature and bias). Pixels are also addressed to control properties [sic: temperature and bias] during post-deposition processing steps such as heating in vacuum or various gases to alter stoichiometry of a single material, or to alloy multiple-composition materials." In context, a person of ordinary skill in the art would have understood such disclosure to teach, at most, varying the stoichiometry of individual materials to the extent such is accomplished by varying the pixel temperature and bias associated

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therewith, or evaluating an alloying process for the same multi-composition material as a function of temperature. Such disclosure would not have taught or suggested to a person of ordinary skill in the art to vary, from region to region, the composition, concentration, stoichiometry, or thickness of the components being delivered to the substrate.

10. The delivery of first and second components in successive layers within discrete regions of a substrate, while varying the composition, concentration, stoichiometry and/or thickness of the delivered components between respective regions of the substrate provides advantages for materials science research involving inorganic and composite materials (e.g., formed by physical vapor deposition). For materials discovery research, both chemical diversity (e.g., composition) and physical diversity (e.g. grain size) can be of substantial importance with respect to effecting commercially-important changes in material properties. Significantly, a substantially larger scope of chemical diversity can be achieved by varying parameters (e.g. composition, etc.) of delivered components as taught by Applicants – as compared to that which could be achieved by varying process parameters as disclosed by Cavicchi *et al.*).

11. The combined teaching of Cavicchi *et al.* and Fister *et al.* would not have taught or suggested to a person of ordinary skill in the art the desirability of creating an array of materials on a common substrate with the extent of chemical diversity effected by the methods defined by independent claims 42, 68, 70, 72, 74, 84 and 88, together with claims depending therefrom. A person of skill in the art would have understood Cavicchi *et al.* as contemplating diversity of materials only to the extent that such diversity is effected by varying temperature or voltage – which are the specifically-taught process parameters. Moreover, Fister *et al.* would have been understood as teaching the benefit of their process to achieve a single homogeneous sample, and as such, a person of ordinary skill in the art would not have looked to modify Fister *et al.* in a manner that would have been contrary to such intended purpose.

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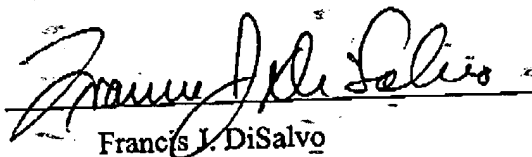
12. The difference between the Applicants claimed methods and those of the prior art are commercially significant, as evidenced by the widespread acceptance and implementation of Applicants methods by various types of research organizations across numerous industrial sectors. Prior to the invention at issue, it was well understood by a person of ordinary skill in the art that, the generally-accepted and followed paradigm for inorganic materials research typically involved bench scale research with individual samples or groups of individual samples, followed pilot plant scale research for materials and methods optimization, and finally commercial scale operations. In contrast, however, the inventions claimed in this application include methods that have, along with other methods, contributed to a true paradigm shift, in that inorganic materials synthesis is now widely pursued using high-throughput combinatorial materials research techniques, including the techniques claimed herein, as a way to create a more promising pipeline of materials prior to entering bench scale and/or pilot plant scale tests.
13. Based on my factual observations and interpretations about what the various references teach (or don't teach), it is my opinion that at a time prior to the present invention, a person of ordinary skill in the art of inorganic materials synthesis would not have been motivated to develop the methods defined by claims 42, 68, 70, 72, 74, 84 and 88, together with claims depending therefrom, from the references cited. The reasons for this opinion relate to deficiencies in the prior art with respect to teaching of required features of the present invention, as discussed above. Additionally, in my opinion, a person of skill in the art would not have been motivated by the Fister *et al.* reference or the Cavicchi *et al.* reference, considered alone or in combination, to modify the teachings thereof in a manner that would have led to these claimed inventions.
14. The inventions claimed in this application have significantly advanced materials discovery efforts, and especially thin-film inorganic materials discovery efforts. In fact, the public disclosure of the inventor's innovations has sparked an entire industry, and motivated further research in combinatorial high-throughput catalysis discovery research. Anecdotaly, notwithstanding the current evidence of the success of this approach to

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inorganic materials and composite materials research, my initial reaction to the teaching of the inventors with respect to applications to inorganic materials was one of considerable skepticism. However, along with others in both academia and the chemical industry, I later realized the significance of the contributions of the inventors to inorganic materials research. Approaches that include the approaches taught in this patent application have revolutionized the way in which discovery research is being done in major corporations and to a lesser extent in academia, as evidenced by the growing body of literature and increasing commercial activity – all following the lead of these inventors.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that the statements herein were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001, and that such willful false statements may jeopardize the validity of the above-identified application or any patents issuing thereon.

Date: Feb. 9, 2003


Francis J. DiSalvo